Direct observation of the break-up of a nocturnal inversion layer using elemental mercury as a tracer

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[1] Concentrations of atmospheric mercury observed during July and August of 2005 in Riverside, CA and during August of 2006 at sites throughout the Los Angeles Basin indicate that a diurnal pattern of elemental mercury frequently exists within the basin during summer months. During these diurnal cycles, elemental mercury is observed to abruptly spike well above global background levels during the morning hours. These peak events were observed to be coincident across several monitoring sites throughout the Basin suggesting that mercury spikes were not a result of source plumes unique to each site but rather the impact of a basin-wide phenomenon. Atmospheric temperature profiles measured by a Radio Acoustic Sounding System (RASS) located in Moreno Valley, CA indicate that peak events coincided with the shift in surface temperature profile from stable to neutral indicating the presence of fumigation episodes, the occurrence of which is supported by a generic model of basin dispersion. The presence of mercury in the stable layer aloft is a function of point sources within the basin, and in particular a single, elevated point source located in the Port of Long Beach. The unique dynamics of atmospheric mercury observed throughout the Los Angeles Basin combined with the location of this major point source upwind of the Basin provide a novel method of directly observing atmospheric mixing associated with the break-up of the nocturnal inversion layer. **Citation:** Snyder, D. C., T. R. Dallmann, J. J. Schauer, T. Holloway, M. J. Kleeman, M. D. Geller, and C. Sioutas (2008), Direct observation of the break-up of a nocturnal inversion layer using elemental mercury as a tracer, *Geophys. Res. Lett.*, *35*, L17812, doi:10.1029/2008GL034840.

1. Introduction

[2] Elemental mercury (Hg^0) is a ubiquitous constituent of the troposphere due to its stability in the atmospheric environment, its low water solubility, and its numerous sources, both natural and anthropogenic. When combined, these factors result in an atmospheric lifetime of 0.5 to 2 years, long enough to permit inter-hemispheric mixing, and a global background concentration estimated to be between 1.5 and 2.0 ng m^{-3} [*Lin and Pehkonen*, 1999]. The notoriety of atmospheric mercury is due to its role as the primary source of mercury to aquatic systems [*U. S. Environmental Protection Agency (EPA)*, 1997]. The link between atmospheric mercury deposition and levels of one of the more bio-available forms of mercury, methylmercury, in the aquatic food web [*Hammerschmidt and Fitzgerald*, 2006] and its associated human and environmental health risks [*Clarkson*, 1993; *Knobeloch et al.*, 2006] have prompted recent regulatory efforts by state and national agencies to decrease the atmospheric emissions of mercury compounds from anthropogenic sources.

[3] While the processes that affect mercury transport are worthwhile to investigate in the context of mercury chemistry and regulation, the work presented here focuses on the utility of mercury as a tracer for general boundary layer processes over Los Angeles. Because diurnal cycles in the boundary layer affect both weather and air quality in the L.A. Basin, direct methods of observing these processes are extremely useful as tools for evaluating atmospheric dispersion models and providing insights into physical processes. In particular, the physical and chemical properties of elemental mercury, the unique meteorology of the Basin, and the location and size of mercury point sources in Los Angeles combine to make Hg^0 a novel tracer for observing atmospheric mixing associated with the break-up of the nocturnal inversion layer. Although the atmospheric dynamics and sources of Hg^0 in other environments may be very different from those in the Los Angeles Basin, thus limiting the use of Hg^0 as a tracer, this work suggests the possibility that novel tracers may be present in other locations providing researchers with alternatives to releasing experimental tracers to validate models and observe atmospheric processes.

2. Experimental Details

2.1. Atmospheric Measurements

[4] Hourly mercury measurements were made daily for four weeks at a single site located in Riverside, CA during the summer of 2005 and at five sites throughout the Los Angeles Basin for two weeks during the summer of 2006 (detailed monitoring dates/times are shown in Table S1 in the auxiliary material).[1] The initial monitoring campaign, conducted in July and August of 2005, took place at the Air Pollution Research Center (APRC) on the campus of the University of California-Riverside in close proximity to the South Coast Air Quality Monitoring District's (SCAQMD)

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Table 1. Mercury Emissions Inventory for the Los Angeles Basin[a]

Facility	Facility Type	Emissions (lbs. yr-1)	% Basin Hg Emissions	Effective Stack Height (m)
1	Incinerator/Metals Reprocessing	1041	61.7	42, 50
2	Cement Kiln	260	15.4	26
3	Electronics Manufacturer	72	4.3	n.a.[b]
4	Petroleum Refinery	70	4.2	120
5	Secondary Lead Smelter	65	3.9	n.a.
6	Cement Kiln	50	3.0	26
7	Electronics Manufacturer	45	2.7	n.a.
Others	Individual Sources Emitting <45 lbs. yr^{-1}	82	4.9	-
Total		1685	100	

[a]Los Angeles, Orange, Riverside, and selected areas of San Bernardino Counties.
[b]n.a. refers to not available.

vertical wind profiler site in Moreno Valley, CA. Subsequent measurements in August of 2006 took place at the University of Southern California's Particle Instrumentation Unit (PIU), located adjacent to downtown Los Angeles, and at four SCAQMD monitoring sites located throughout the Basin (Los Angeles International Airport, Wilmington, Anaheim, and Azusa).

[5] Concentrations of atmospheric elemental mercury were obtained using a commercially available mercury monitor (Tekran model 2537A). Details on the use and validation of this instrument are available in detail elsewhere [*Schroeder et al.*, 1995] and will only be briefly discussed here. The instrument collects mercury vapor on cartridges packed with an ultra-pure gold adsorbent and then thermally desorbs the cartridges under a stream of ultra-high purity (UHP) argon gas. Mercury vapor is then analyzed by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS), an ultra-trace level detection technique capable of quantifying mercury at sub ng m^{-3} (parts-per-trillion or lower) levels. The monitor utilizes a matched pair of cartridges to provide a continuous data stream with a time resolution of five minutes.

[6] Vertical temperature profiles were obtained using a 915-MHz Lower Atmospheric Profiler (LAP 3000, Vaisala Corporation, Louisville, CO) with a Radio Acoustic Sounding System (RASS) located in Moreno Valley, CA 15 km from the UC-Riverside monitoring site. A detailed description of this type of instrument is given by *Martner et al.* [1993]. Contemporaneous measurements of ozone (O_3) and carbon monoxide (CO) were made in Riverside during the 2005 monitoring campaign using EPA Designated Reference or Equivalent Methods [*U.S. EPA*, 2005].

2.2. Atmospheric Dispersion Modeling

[7] Elemental mercury concentrations were predicted using the UCD/CIT source-oriented photochemical transport model [*Kleeman and Cass*, 2001; *Ying et al.*, 2007]. For the purposes of this study, the model considered pollutant emissions, advection, and turbulent mixing only. While deposition processes, gas-phase reactions, and gas-to-particle conversion are important to modeling atmospheric mercury in locations away from large sources, the current understanding of reaction kinetics and dry deposition rates for elemental mercury indicate these processes are generally much too slow to significantly impact Hg^0 concentrations in areas adjacent to major sources [*Lin and Pehkonen*, 1999; *Lin et al.*, 2006], which supports the simplifications used in this model run. The purpose of including the dispersion modeling in this work is to confirm that emissions inventory data support the mercury concentrations observed within the basin and to provide additional evidence of the unique dynamics of mercury within the Basin. Detailed information concerning the application of this model can be found in the auxiliary material accompanying this paper.

3. Results and Discussion

[8] Given the absence of two of the most prolific sources of atmospheric mercury, coal-fired power plants and medical waste incinerators, the Los Angeles Basin seems at first glance an unlikely location to observe elevated concentrations of elemental mercury. However, emissions inventory data (Table 1) reveal that mercury emissions from point sources located in the Basin total nearly 1700 lbs. yr^{-1} or nearly 1% of the total U.S. atmospheric mercury emissions, which were estimated at 109.2 tons in the year 2000 [*Pacyna et al.*, 2006]. Emissions from a single point source, an incineration and metals reprocessing facility located adjacent to the Port of Long Beach, contribute greater than 60 percent of atmospheric mercury emanating from point sources in the Los Angeles area and greater than 10 percent of the total point source emissions from the state of California [*U.S. EPA.*, 2007a] (accessed on August 27, 2007). The location of this facility, labeled as facility # 1, along the shoreline (Figure 1) where its emissions can be dispersed by the prevailing winds places it in a position to strongly influence mercury concentrations across the Basin.

[9] As might be predicted by the quantity of mercury emanating from sources within the Los Angeles Basin, concentrations of elemental mercury observed during July and August of 2005 in at the Riverside, CA monitoring site were consistently well above the global background level of 1.5–2.0 ng m^{-3} [*Lin and Pehkonen*, 1999; *Schroeder and Munthe*, 1998]. Five-minute Hg^0 concentrations averaged 2.98 ng m^{-3} and reached a maximum of 9.38 ng m^{-3} but more significantly, demonstrated a diurnal pattern in which mercury concentrations spiked sharply during the morning hours (Figure 2). This pattern might at first glance appear to be the impact of a mercury 'plume' being emitted by a nearby point source; however, when the observed mercury concentrations are compared with concentrations of carbon monoxide (CO), an indicator combustion activity, a poor correlation is seen (linear regression $R^2_{CO} = 0.05$, Figure S1)

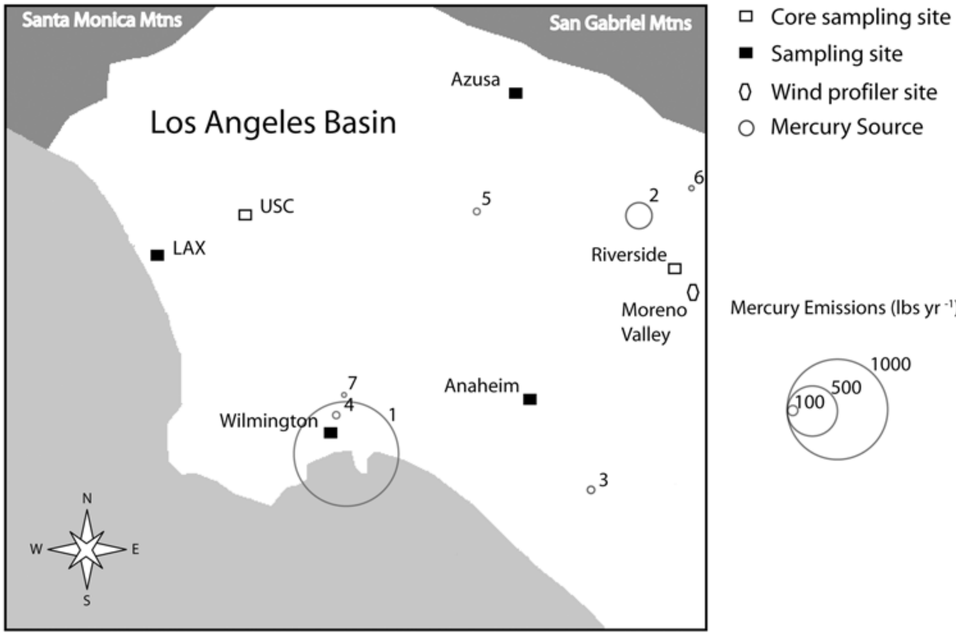

Figure 1. A graphic representation of the Los Angeles Basin reveals the emission rates and locations of the major mercury emitting sources within the Basin and their proximity to the 2005 study site in Riverside and the 2006 study sites at USC, LAX, Wilmington, Anaheim, and Azusa.

suggesting that the observed mercury spikes are not a result of a local source plume.

[10] Subsequent to the Riverside monitoring campaign, a series of experiments were conducted in August of 2006 to determine the origin of the observed diurnal mercury cycle. During these experiments, a core monitoring site was established on the campus of The University of Southern California adjacent to downtown Los Angeles. In conjunction with the mercury measurements taken at this site, secondary sites were established at four locations throughout the basin (Figure 1) at which elemental mercury concentrations were monitored sequentially using a second instrument for two days at each site. As can be seen in Figure 3, a diurnal pattern of mercury concentrations was again observed at the core monitoring location, and this pattern was mirrored at each of the secondary monitoring sites supporting the conclusion that the observed mercury cycle was a result of a basin-wide phenomenon and not point source plumes unique to each site.

[11] In order to assess the impact of Basin meteorology on the dispersion of mercury, meteorological data were obtained for Riverside for the 2005 monitoring period including 5 meter wind speed and direction and vertical temperature data obtained from the nearby Moreno Valley

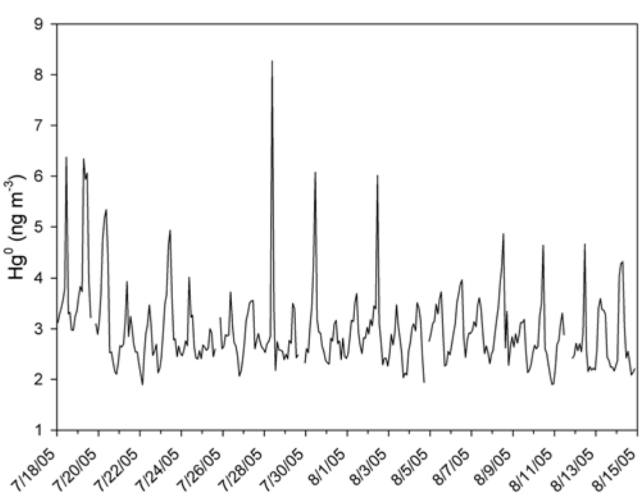

Figure 2. A time series of elemental mercury concentrations observed during July and August of 2005 in Riverside, CA reveals that Hg^0 levels consistently remain well above the global background and exhibit a pronounced diurnal pattern.

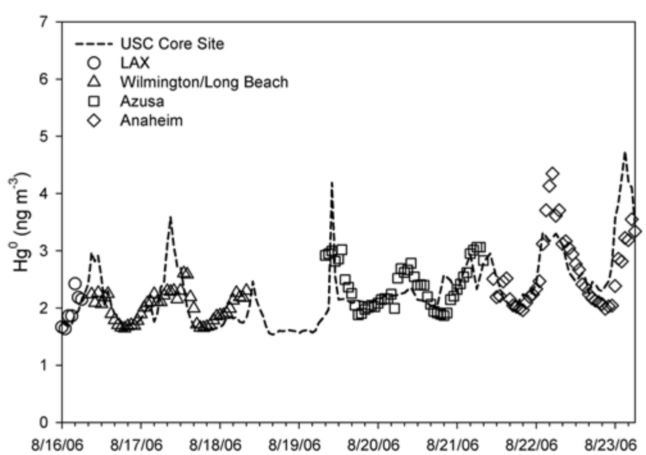

Figure 3. During July of 2006, a diurnal pattern of mercury concentrations was observed at a monitoring location on the campus of the University of Southern California, adjacent to downtown Los Angeles (dashed lines). This pattern was mirrored at four other monitoring sites (symbols) spread throughout the Basin.

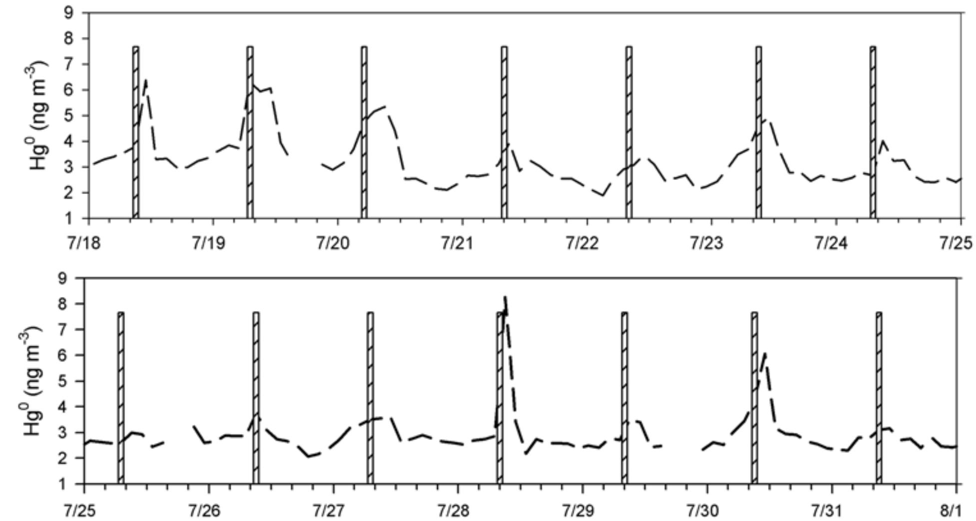

Figure 4. A strong correlation between the time at which the break-up of the nocturnal inversion layer occurs (black bars) and the incidence of elemental mercury spikes in Riverside, CA supports the conclusion that these spikes represent fumigation episodes in which mercury trapped during evening hours in the stable layer aloft is rapidly mixed towards the surface as the temperature profile shifts from stable to neutral.

SCAQMD wind profiler site. Surface data indicated that mercury spikes observed in Riverside during the summer of 2005 occurred when winds were from the west (see Figure S2) when the monitoring site was directly downwind of the source located in Long Beach. Simple Gaussian plume models were run to see if the direct impact of a plume traveling from Long Beach to Riverside through the mixed layer might produce the observed mercury spikes. Following *Seinfeld and Pandis* [1998], models were run for all Pasquill stability classes and considered source strengths from one to one thousand times the annual mercury emission rate attributed to the source located in Long Beach. Model predictions only equaled or exceeded peak mercury concentrations observations in Riverside on the plume centerline, at low wind speeds, stable conditions, and when 1000 times the emissions rate was used. While it is not inconceivable that such conditions might occur, they are unlikely to occur with the frequency of the observed mercury spikes especially given the diurnal temperature gradients and peak temperatures (exceeding 100 degrees Fahrenheit) observed during the study period. For all other model runs, mercury concentrations predicted by the Gaussian Plume model did not exceed the background levels observed in Riverside. These results indicate the likelihood that the observed mercury spikes resulted from some other process such as the transport of mercury in the stable layer aloft in which limited vertical dispersion occurs, a phenomenon previously observed with regards to ozone concentrations in Southern California and the northeastern United States [*Bigler-Engler and Brown*, 1995; *Zhang and Rao*, 1999].

[12] Vertical temperature profiles constructed from the Moreno Valley RASS data indicate the frequent presence of a nocturnal inversion layer over the Los Angeles Basin during the 2005 monitoring period. A representative example of these profiles is shown in the auxiliary material accompanying this paper (Figure S3) which also shows the break-up of the inversion layer as the temperature profile, also known as the environmental lapse rate (ELR), approaches the dry adiabatic lapse rate (DALR), the rate at which a dry parcel of air cools with increasing altitude. When the ELR matches the DALR, rapid vertical mixing can occur resulting in a sharp increase in the surface concentrations of species, mercury emitted by point sources within the Basin in this case, trapped above the inversion height during the evening hours.

[13] By analyzing the vertical temperature profiles for the 2005 Riverside monitoring period, the timing of the break-up of the nocturnal inversion layer was determined for each day. When these data are placed on a time series of elemental mercury (Figure 4), the observed elemental mercury spikes and the break-up of the inversion layer appear coincident supporting the presence of fumigation episodes. The observation that mercury spikes vary in intensity and duration indicates that these episodes can be directly affected by other meteorological variables, such as wind speed and direction, or by variations in mercury emission rates from the source. The specific causes for this variability are beyond the scope of this paper, but the unique character of these events provides a unique set of observations against which Basin dispersion models can be compared.

[14] As an additional confirmatory measure, point source information contained in Table 1 was used to model mercury concentrations across the Los Angeles Basin using the UCD/CIT source-oriented photochemical transport model. Available meteorological data from September, 1996 was used [*Kleeman and Cass*, 2001], and although the model utilizes data from a time period significantly removed from the study periods so that no direct comparisons between observations and models could be made, the results support the observation that emissions attributed to point sources within the LA Basin may produce significantly elevated elemental mercury concentrations at or near the study sites (Figure S4). In addition, the model indicates the presence of a mercury spike in Anaheim similar to those observed during the summer of 2006 (Figure S5). Although

temperatures profiles were not available to confirm whether the predicted episode is a result of the same fumigation processes that were observed during the study periods, model calculations effectively predict a ground-based inversion during evening hours due to low wind speeds and an absence of solar heating. Enhanced mixing can be expected to occur during the day as solar heating produces warmer air near the surface that rapidly mixes upwards and increased wind speed generates mechanical turbulence. In the current model study, nighttime ground based inversions transitioned to mixing depths $\geq$ 800m during the late morning/early afternoon, depending on location, suggesting that the modeled mercury spike represents a likely fumigation episode.

[15] Combined with the model results, the observations made during this study suggest that the dynamics of elemental mercury within the Los Angeles Basin represent a unique opportunity to directly observe atmospheric processes across the Basin. Clearly, the dynamics of atmospheric mercury in the Los Angeles area are somewhat unique, suggesting that the use of mercury as a tracer may not be applicable in other urban environments; however, this work suggests that it may be worthwhile to explore the possibility that mercury and other compounds already present in the atmosphere may be suitable as tracers to directly observe physical processes and validate models without the need to release experimental compounds.

[16] **Acknowledgments.** The authors wish to acknowledge the significant contributions made to this work by the SCAQMD, Mark Olson at the USGS, Paul Ziemann at UC-Riverside, and Ken Docherty and Jose-Luis Jimenez at CU-Boulder.

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